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13. ABSTRACT (Maximum 200 words) Changes in refractive index achieved by photodeposition and their transmissivity depend on the nature of the material deposited, its aggregation and its effect on the host matrix. 254-nm photolysis of $(CH_3)_3SnI$ chemisorbed onto porous Vycor glass and Si-based sol-gel glasses leads to homolytic cleavage of the Sn-I bond. Depending on medium polarity, a fraction of the radical pairs thermalize via electron transfer and $(CH_3)_3SN^+$, which is converted to SnO during the subsequent annealing, changes the refractive index. During consolidation, Sn and/or SnO displace boron from the matrix, and the corresponding change in glass composition opens a 100-150°C window that has been exploited to introduce reagents that are unable to withstand glass processing temperatures into an optical network in glass. Ferromagnetic impregnates exhibiting extremely high coercivity obtained by photolysis of $Fe(CO)_5$, have been shown to be 100 ^Å diameter particles of $\alpha-Fe_3O_4$, where particle size is determined principally by the initial pore size of the glass. A technique has been developed to pattern micron-resolution, transparent, electrically conductive regions on porous glasses without significant reductions in glass porosity. During the course of these experiments, a new type excited-state coordination chemistry has been discovered.					
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Department of Defense Air Force Office of Scientific Research Final Project Report

Part I Project Identification Information

Program Official/Org.	Charles Lee
Program Name	BMDO Science and Technology
Award Dates	From: 4/94 To: 3/97
Organization and Address	Research Foundation of the City University of New York 30 West Broadway New York, NY 10003
Award Number:	F-49620-94-1-0209
Project Title	Photodeposition in Porous Glass

Part II.a Summary of Completed Project

Photodeposition of metals and metal oxides in porous glasses followed by thermal consolidation to a nonporous glass changes the refractive index of the glass. The gradient achieved and its transparency, however, depend on the nature of the species deposited, its aggregation, and its effect on the host matrix. Two molecules were examined in detail; $(\text{CH}_3)_3\text{SnI}$ and $\text{Fe}(\text{CO})_5$ since the photoproducts of the former curtail the consolidation of the glass, while the latter yield magnetic

impregnates. $(\text{CH}_3)_3\text{SnI}$ chemisorbs onto porous Vycor glass (PVG) by reacting with a surface silanol group to form a surface bound five coordinate species. Photolysis of the latter yields Sn and SnO , and one or both of these species displace boron from the glass matrix. Boron diffuses to the glass surface where it reacts with water vapor to form crystalline H_3BO_3 which, as previously observed, changes the morphology of the glass surface. Loss of boron also changes the composition of the glass, and in turn its viscosity. The increased viscosity curtails the rate of consolidation of the porous glass, and in the regions containing the photodeposited tin, opens a 100-150°C window that is exploited to retain patterns of porosity within an otherwise consolidated glass.

Mono- and bi-metallic Ru(II) dimines were used as luminescent probes of the microenvironment within these photopattern porous regions. These experiments led to the discovery of a very unusual photochemical reaction. In contrast to the well established photoinduced redox degradation or ligand substitution found with most coordination compounds, an entirely new photoreaction that yields a product of higher metal content than the reactants, and more surprising, is quantitative through $\geq 70\%$ conversion. Preliminary experiments suggest a new type of quenching mechanism where excitation changes the acid-base properties of one reactant, and these changes, specifically an enhancement in basicity by *ca.* five orders of magnitude, result in an excited state coordination chemistry.

The photoproducts derived from $\text{Fe}(\text{CO})_5$ do not affect the consolidation of the glass. Instead, the glass morphology, specifically the average pore size and the average spacing between the pores, determines photoproduct particle size, and in turn, the particle's magnetic properties. $\text{Fe}(\text{CO})_5$ physisorbs onto PVG and photolysis in air yields Fe and FeSiO_4 as the primary photoproducts. No particles of $\geq 10\text{D}$ in diameter. Heating the samples in air removes the unreacted $\text{Fe}(\text{CO})_5$ and yields a mixture of Fe° and $\alpha\text{-Fe}_2\text{O}_3$. Further heating in air to 650°C does not substantially change the amount of elemental iron present suggesting that the elemental iron particles become covered with Fe_2O_3 preventing further oxidation. Initially, the particles are $\leq 10\text{D}$, but increase to 35-40D in diameter during heating. The increase in particle size does not change the relative amounts of Fe° and $\alpha\text{-Fe}_2\text{O}_3$, and at this point, the particles exhibit superparamagnetism. Heating the samples to 1200°C in air consolidates the glass matrix. There is no change in the composition of the impregnate, but the particle size increases to $100 \pm 10\text{D}$ in diameter with an average spacing between the particle of *ca.* 200D. The final particles formed in the consolidated glass are ferromagnetic and exhibit a large coercivity. Since the final particle size does not increase with increasing initial $\text{Fe}(\text{CO})_5$ loading, particle size and spacing are controlled by the morphology of the initial porous matrix. The particle diameters in the consolidated glass are identical to the initial pore size in the glass, $100 \pm 10\text{D}$, and the spacing between the particles, *ca.* 200D is within experimental error of the correlation length, $242 \pm 30\text{D}$, of the initial porous glass.

Concurrent with the characterization experiments, prototype devices have been assembled. Techniques have been developed to pattern, micron resolution, transparent, electrically

conductive coatings onto porous glass without a significant decline in the glass porosity. These techniques achieve micron resolution, indium-tin oxide pattern with a resistance of ca. 100 ohms/square. The coatings, which extend 5-10 microns into the porous glass, have no effect on the transparency of the glass and parallel the glasses transparency from 300 nm to 2000 nm. Glasses with interdigitated patterns of electrically conductive regions have been produced. These devices will be impregnated with piezoelectric polymers to determine the feasibility of gratings whose optical transmission properties are determined by an applied voltage rather than a mechanical movement.

Techniques have been developed to photochemically deposit diffraction gratings by conventional photochemical and holographic photochemical techniques have been developed. Conventional phase gratings are prepared by the photodeposition of $\alpha\text{-Fe}_2\text{O}_3$ using a micron resolution computerized stage. The computer programming to drive the stage has been written, and resolution of the resultant device determined by microscopic analyses and corroborated by light diffraction measurements. These experiments establish that the resolution of the grating, i.e., the line spacing, is not lost during consolidation, but actually improved by a factor corresponding to the decrease in sample dimension perpendicular to the refractive index gradients. The resolution of this conventional technique is limited by light scattering from the initial porous glass. A holographic approach has been developed, and the resolution achievable by this technique, and the diffraction properties of the resulting holographic gratings are currently being compared to those of the conventional phase gratings.

Part II.b. Human Resource Development.

This NSF grant has supported the thesis research of Ph.D. students Charles Hicks, Anthony Maletta, Clement Tsang, Jinqun Dong, Guozhang Ye as well as the postdoctoral studies of Sujatha Devi, Chaim Levi and Delaphawalage Sunil. Mr. Hicks and Mr. Ye are continuing their Ph.D. studies in the lab along with Drs. Sunil and Levi. Dr. Devi returned to India with her husband, and Mr. Maletta got married and transferred to SUNY-Stony Brook to complete his Ph.D. in physical chemistry since his wife is in the biochemistry Ph.D. program there. Jinqun Dong received his Ph.D. in physical chemistry this past September and is employed as a research scientist at Anderson Paper and Coatings on Long Island. Clement Tsang is currently writing his thesis and expects to complete his Ph.D. in physics this winter. He is currently employed as a computer software specialist at Market Data in Rye Brook, NY. Queens College undergraduates Joe Lawler and Josh Bergman, currently enrolled in the M.D.-Ph.D. Program at Johns Hopkins and dental school, respectively, carried out summer research under the auspices of this grant. In addition to the Queens undergraduates, collaborations with Professors Irina Rutenburg and Peter Wong of Queensborough Community College, and Jainwei Fan, a former student and currently an Assistant Professor at Manhattan College, have allowed four undergraduates from these institutions to carry out summer research in this laboratory. These undergraduates prepare sol-gel glasses, or coordination compounds at their

home institutions, and then examine the properties of the glasses or compounds at the Queens College laboratories. In addition to Mr. Dougherty, Dr. Arthur McQuade, who teaches physics at New Rochelle High School, has been examining the photodeposition of conventional and holographic gratings in glass under the auspices of this grant and a College sponsored summer research program for the past two years.

Part III Technical Information

Publications Resulting from DOD/AFOSR Award.

Gafney, H. D.; Pillion, J. E.; Rafailovich, M. H.; Sokolov, J.; Sunil, D.; O'Connor, C. J.; Thompson, M. E. "Intercalation Induced Reactions of Iron Oxychloride" *J. Solid State Chem.* (1994), 113, 261.

Describes the characterization of the intercalated iron oxychloride.

Gafney, H. D.; Fan, J.; Tysoe, S.; Strekas, T. C.; Lawless, D.; Serpone, N. "Excited State Dynamics of Ru(bpy)₃²⁺ on Porous Vycor Glass. Intervention of a Ligand Localized Triplet State", *J. Am. Chem. Soc.* (1994), 116, 5343.

Describes the photophysical properties of of this luminescent complex in porous glass. Although it is generally accepted that the intersystems crossing in this complex is independent of temperature, data presented in this publication show that the intersystems crossing of the adsorbed complex is temperature dependent. Hence, it use as a luminescent probe of microenvironment must recognize this fundamental change in its photophysical properties.

Gafney, H. D.; Braun, M. "Photoinduced Electron Transfer in Porous Glass" *J. Phys. Chem.* (1994), 98, 8108.

A mathematical model treating electron migration on the glass as the probability of encountering another reactant as opposed to recombination is described. The calculation reinforce the idea that electron conduction on these glasses is a surface phenomenon with teh photodetached electron populating shallow surface traps from which it can be thermally ejected.

Gafney, H. D.; Fan, J. "An Examination of the Role of B₂O₃ Lewis Acid Sites in Electron Transport on Porous Vycor Glass" *J. Phys. Chem.* (1994), 98, 13058.

Two photon excitation of Ru(bpy)₃²⁺ cation exchanged into porous Vycor glass causes ionization and electron injection onto the glass surface. Electron conduction on the glass surface is thought to occur via a surface conduction process where the ionized electron populates shallow

surface traps. One possibility are the boron oxide Lewis acid sites on the glass surface. However, selective adsorption experiments show that these sites are not involved in the electron transport, but instead are irreversible electron traps.

Gafney, H. D.; Sunil, D.; Rafailovich, M.; Sokolov, J. "Inorganic Chemistry in Integrated Optics" in the Second Nassau Mossbauer Conference, Wynter, C. I.; Alp, E. E. Ed., W. C. Brown, DuBuque, IA, 1995, p. 145.

A review of the photodeposition of gradient indices in porous glasses.

Gafney, H. D.; Xu, S.-P. "Photocatalyzed Isomerization of 1-Pentene by $\text{Ru}_3(\text{CO})_{12}$ Adsorbed Onto Porous Vycor Glass" *Inorg. Chim. Acta*, (1995) 240, 645.

Describes the photocatalyzed isomerization of 1-pentene by $\text{HRu}_3(\text{CO})_{10}(\text{OSi})$, which is the primary photoproduct of $\text{Ru}_3(\text{CO})_{12}$.

Gafney, H. D.; Dong, J. "Fabrication and Patterning Surface Electrically-Conductive Porous Glass" *J. Non-Crystal. Solids*, (1996), 203, 329.

Describes the fabrication and patterning of transparent, electrically conductive coatings on porous glasses.

Gafney, H. D.; Devi, P. S.; Petricevic, V.; Alfano, R. R. "Sol-Gel Synthesis and Characterization of Metal-Ion (Cr^{4+}) Doped Luminescent Glasses and Their Applications" *J. Non-Crystal. Solids*, (1996), 203, 78.

Describes the synthesis and spectroscopic properties of Cr^{4+} doped porous glasses prepared by sol-gel techniques.

Gafney, H. D.; Sunil, D.; Tsang, C.; Sokolov, J.; Rafailovich, Gambino, R. J.; Huang, D. M. "Magnetic Properties of Nanoscale Iron Particles Photodeposited in Glass", *Mater. Res. Soc. Symp. on "Surface/Interface and Stress Effects in Electronic Material Nanostructure"*, (1996), 405, 0000.

A summary of the magnetic properties of iron doped porous glasses.

Gafney, H. D.; Sunil, D.; Rafailovich, M.; Sokolov, J.; Gambino, R. J., Tsang, C.; Huang, D. M. "High Coercivity Single-Domain Particles in Glass Matrix", *J. Appl. Phys.* (1996), 79(8), 6025.

Describes the magnetic properties of iron doped porous glasses as a function of annealing conditions.

Gafney, H. D.; Miyano, K. E.; Woicik, J. C.; Huang, D.; Devi, P. S. "Cr-K-Edge X-ray Absorption Study of Cr Dopants in Mg_2SiO_4 and Ca_2GeO_4 ", *Appl. Phys. Lett.* (1997), 71, 1168.

Describes EXAFS and XANES techniques to determine the oxidation state of chromium doped into porous glasses.

Gafney, H. D. "A Photochemical Approach to Integrated Optics" in "*Chemistry in Industry*", Perry, D. Ed. Plenum Press, New York, (1997) p. 189.

Describes optical elements created by photodeposition in porous glasses.

Gafney, H. D.; Hicks, C.; Fan, J.; Rutenberg, I. "Excited State Acid-Base Chemistry A New Quenching Mechanism" *Coord. Chem. Revs.* (1997), in press.

Describes a new type of bimolecular quenching process based on changes in acid-base properties that accompany optical excitation.

Gafney, H. D.; Dougherty, T.; Hicks, C.; Maletta, A.; Fan, J.; Rutenberg, I. "Excited State Acid-Base Chemistry A New Quenching Mechanism" *J. Amer. Chem. Soc.* (1997), in press.

Describes a new type of bimolecular quenching process where changes in acid-base properties that accompany optical excitation leads to quenching via changes in coordination as opposed to electron or energy transfer.

Gafney, H. D.; Dong, J.; Devi, S.; Mendoza, E. "Photodecomposition of Iodotrimethylstannane Adsorbed on Porous Vycor Glass" *Inorg. Chem.*, submitted.

Describes the photochemistry of iodotrimethylstannane adsorbed onto porous Vycor glass.

Gafney, H. D.; Sunil, D.; McQuade, A. W. "Photodeposition of Diffraction Gratings in Glass" *Appl. Spectrosc.*, submitted.

Describes the photodeposition of phase grating in porous glass and their properties before and after consolidation.

Patent Disclosure:

Gafney, H. D. "A Photochemical Technique for Patterning Porosity in Glass", Disclosed to the Research Corporation, 4/94.

Harry D. Gelfand

Principal Investigator/Project Director Signature

1 12/15/97

Date

PART IV - FINAL PROJECT REPORT — SUMMARY DATA ON PROJECT PERSONNEL

(To be submitted to cognizant Program Officer upon completion of project)

The data requested below are important for the development of a statistical profile on the personnel supported by Federal grants. The information on this part is solicited in response to Public Law 99-383 and 42 USC 1885C. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. You should submit a single copy of this part with each final project report. However, submission of the requested information is not mandatory and is not a precondition of future award(s). Check the "Decline to Provide Information" box below if you do not wish to provide the information.

Please enter the numbers of individuals supported under this grant.

Do not enter information for individuals working less than 40 hours in any calendar year.

	Senior Staff		Post-Doctorals		Graduate Students		Under-Graduates		Other Participants ¹	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
A. Total, U.S. Citizens	1				2		2	4	2	
B. Total, Permanent Residents			2		3					
U.S. Citizens or Permanent Residents ² :										
American Indian or Alaskan Native . . .										
Asian							2			
Black, Not of Hispanic Origin							1			
Hispanic										
Pacific Islander										
White, Not of Hispanic Origin										
C. Total, Other Non-U.S. Citizens										
Specify Country										
1. <u>India</u>				1						
2.										
3.										
D. Total, All participants (A + B + C)	1		2	1	5		2	4	2	

Disabled³

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¹Category includes, for example, college and precollege teachers, conference and workshop participants.

²Use the category that best describes the ethnic/racial status to all U.S. Citizens and Non-citizens with Permanent Residency. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

³A person having a physical or mental impairment that substantially limits one or more major life activities; who has a record of such impairment; or who is regarded as having such impairment. (Disabled individuals also should be counted under the appropriate ethnic/racial group unless they are classified as "Other Non-U.S. Citizens.")

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America and who maintains cultural identification through tribal affiliation or community recognition.

ASIAN: A person having origins in any of the original peoples of East Asia, Southeast Asia or the Indian subcontinent. This area includes, for example, China, India, Indonesia, Japan, Korea and Vietnam.

BLACK, NOT OF HISPANIC ORIGIN: A person having origins in any of the black racial groups of Africa.

HISPANIC: A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

PACIFIC ISLANDER: A person having origins in any of the original peoples of Hawaii, the U.S. Pacific territories of Guam, American Samoa, and the Northern Marianas; the U.S. Trust Territory of Palau; the islands of Micronesia and Melanesia; or the Philippines.

WHITE, NOT OF HISPANIC ORIGIN: A person having origins in any of the original peoples of Europe, North Africa, or the Middle East.